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**Determination of aragonite trace element distribution coefficients from speleothem  
calcite-aragonite transitions**

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**Abstract:**

The processes that govern the incorporation of (trace) elements into speleothems can often be linked to environmental changes. Although element incorporation into speleothem *calcite* is now reasonably well understood, current knowledge regarding trace element variability in speleothem *aragonite* is very limited. Of particular interest is whether trace element distribution coefficients are above or below one in order to assess the extent to which prior aragonite precipitation has affected speleothem aragonite trace element records.

This study uses nine calcite-to-aragonite transitions in seven speleothems from diverse environmental settings to derive the first quantitative estimates of the distribution coefficients for several elements in speleothem *aragonite*:  $D_{\text{Mg}(\text{Ar})} = 9.7\text{E-}5 \pm 9.01\text{E-}5$ ,  $D_{\text{Ba}(\text{Ar})} = 0.91 \pm 0.88$ ,  $D_{\text{Sr}(\text{Ar})} = 1.38 \pm 0.53$ , and  $D_{\text{U}(\text{Ar})} = 6.26 \pm 4.54$  ( $1\sigma$  SD). For one speleothem from western Germany, the distribution coefficients are generally higher, which is potentially related to the very low growth rates ( $<11 \mu\text{m/year}$ ) of this sample. In particular,  $D_{\text{Sr}(\text{Ar})}$  appears to show a negative correlation with growth rate when growth rate is below  $20 \mu\text{m/year}$ .

In summary, our results demonstrate that speleothem aragonite  $D_{\text{Mg}(\text{Ar})}$  is below one,  $D_{\text{U}(\text{Ar})}$  is considerably above one, and  $D_{\text{Sr}(\text{Ar})}$  is above one or close to unity. For  $D_{\text{Ba}(\text{Ar})}$ , reaching a similar conclusion is difficult due to the relatively high uncertainty. Enhanced prior aragonite precipitation will thus result in lower U and higher Mg concentrations in speleothem aragonite, although in many cases Mg in speleothem aragonite is most likely dominated by other processes. This result suggests that U concentrations in aragonitic stalagmites could serve as a very effective proxy for palaeo-rainfall.

## 1. Introduction

Speleothems are secondary cave deposits mainly consisting of calcite or aragonite with calcite being the more common polymorph of  $\text{CaCO}_3$  (Hill and Forti, 1997). Speleothems, and in particular stalagmites and flowstones are considered as some of the most promising continental climate archives. They can serve as benchmarks, which can be reliably contrasted and compared with proxy records from complementary archives, because they can be precisely dated up to about 500 ka by the  $^{230}\text{Th}/\text{U}$ -dating technique (e.g., Scholz and Hoffmann, 2008). In addition, speleothem archives can be sampled and analysed with up to sub-annual resolution for carbon and oxygen isotopes (Mattey et al., 2008; McDermott, 2004; Myers et al., 2015) and trace and major elemental abundances (Fairchild and Treble, 2009). Numerous studies on speleothem calcite trace element compositions have been published recently (Borsato et al., 2007; Day and Henderson, 2013; Fairchild and Treble, 2009; Griffiths et al., 2010; Treble et al., 2005; and references therein). Few studies, however, focus on trace element compositions in aragonite speleothems (Finch et al., 2003; Finch et al., 2001; McMillan et al., 2005; Tan et al., 2014; Wassenburg et al., 2012; Wassenburg et al., 2013). The knowledge on element partitioning into speleothem aragonite is thus very limited.

Since aragonite speleothems contain much more U compared to their calcitic counterparts, they can provide excellent age models (Cosford et al., 2008; Myers et al., 2015; Ridley et al., 2015). However, aragonite is metastable and may recrystallize to calcite under certain conditions, which results in post-depositional open system behaviour of the U-series system and apparently incorrect  $^{230}\text{Th}/\text{U}$ -ages (Lachniet et al., 2012; Ortega et al., 2005). Where robust evidence that an aragonite speleothem is well preserved is available (Myers et al., 2015; Wassenburg et al., 2013), the potential to obtain exceptionally precise chronologies is high. Consequently, it is important to further investigate (i) how trace elements partition into speleothem aragonite and (ii) which controls and processes are reflected by their temporal and spatial variability.

The major crystallographic difference between calcite and aragonite lies in their different crystal structures. Aragonite is characterized by an orthorhombic crystallography, where the Ca-ion is coordinated by nine O-ions, whereas calcite has a trigonal crystallography, where the Ca-ion is coordinated by six O-ions (Swart, 2015). Due to these crystallographic differences, larger cations, such as Sr, Ba and U, are preferentially incorporated into aragonite, whereas calcite also tends to incorporate small cations, such as Mg. The corresponding trace element distribution coefficients,  $D_X$ , are defined as:

$$D_X = \frac{X/Ca_{Solid}}{X/Ca_{Solution}}, \quad (1)$$

where X represents a certain trace element. Due to the crystallographic differences, the distribution coefficients may be very different for calcite and aragonite.

Recently, Stoll et al. (2012) introduced a model that facilitates quantitative interpretations of speleothem calcite Mg, Ba, and Sr signals in terms of prior calcite precipitation (PCP) (Fairchild et al., 2000). This process refers to the precipitation of calcite before the dripwater reaches the stalagmite (Fairchild and Treble, 2009), which occurs when the dripwater encounters empty voids within the karst with a lower partial CO<sub>2</sub> pressure compared to the water. This forces degassing of CO<sub>2</sub>, temporarily increasing supersaturation with respect to calcite and calcite precipitation. PCP usually refers to calcite precipitation in the aquifer above the cave, although it may also occur inside the cave (e.g., at the cave ceiling or on the surface of a stalactite). Certain environmental conditions may favour prior aragonite precipitation (PAP) instead of PCP. Fairchild and Treble (2009) first mentioned PAP, which was subsequently documented and detailed by Wassenburg et al. (2013). Both PCP and PAP are enhanced during periods of reduced aquifer recharge when more time is available for degassing and more air-filled voids exist in the aquifer. If trace element distribution coefficients are below (above) one, elevated concentrations in speleothems are typically interpreted as reflecting reduced (enhanced) infiltration and drier (wetter) climatic conditions (Johnson et al., 2006). However, cave ventilation may also control PCP (Sherwin and Baldini, 2011; Wong et al., 2011).

Quantitative and qualitative interpretations of speleothem trace element records strongly depend on well constrained D<sub>X</sub> values. Laboratory precipitation experiments indicate that for calcite, temperature might affect D<sub>Mg(Cc)</sub> (Day and Henderson, 2013; Oomori et al., 1987). Other experiments suggest that precipitation rates (Gabitov et al., 2014; Lorens, 1981; Tesoriero and Pankow, 1996) and/or solution composition (Mucci and Morse, 1983; Pingitore and Eastman, 1986) may control D<sub>Mg(Cc)</sub>, D<sub>Sr(Cc)</sub>, and D<sub>Ba(Cc)</sub>. For aragonite, temperature may affect trace element distribution coefficients for Mg, Ba, and Sr (Dietzel et al., 2004; Gaetani and Cohen, 2006), whereas precipitation rates may influence aragonite distribution coefficients for U and Mg (Gabitov et al., 2008).

However, most of these experiments were designed to reflect marine environments. Within cave environments, the conditions driving CaCO<sub>3</sub> precipitation are very different. Spelean CaCO<sub>3</sub> precipitation is driven by rapid degassing of CO<sub>2</sub> from thin water films (Hansen

et al., 2013) with low ionic strength and the presence of (organic) colloidal phases (Fairchild and Treble, 2009; Hartland et al., 2014), whereas marine deposition occurs in high ionic strength waters and is often biologically mediated. The same arguments prompted a series of studies that aimed to determine speleothem calcite  $D_x$ . These were based on both field precipitation experiments, during which the trace element composition of calcite formed within a cave over a known time period is compared with the trace element composition of the associated dripwater (Fairchild et al., 2010; Gascoyne, 1983; Huang et al., 2001; Karmann et al., 2007; Riechelmann et al., 2014; Tremaine and Froelich, 2013), and cave analogue laboratory experiments (Day and Henderson, 2013; Huang and Fairchild, 2001). These experiments demonstrate that  $D_x$  values determined under karst analogue conditions are different from those in marine environments. Consequently,  $D_x$  values determined under marine conditions are not necessarily transferable to karst settings, and doing so may lead to incorrect climate interpretations.

Karst analogue experiments aiming to determine  $D_x$  values for aragonitic stalagmites have not been performed yet. Thus, these values remain almost entirely unknown. For speleothem aragonite, only one  $D_{Sr(Ar)}$  estimate is available, which is based on modern dripwater Sr/Ca ratios corresponding to an actively growing stalagmite, the Sr concentration at the top of the calcitic stalagmite and the ratio of the Sr content of a calcite and an aragonite phase that precipitated approximately 900 years ago (McMillan et al., 2005). In order to advance the present understanding, we analyse published (McMillan et al., 2005; Wassenburg et al., 2012) and new trace element data from calcite-aragonite transitions in speleothems to derive speleothem aragonite  $D_{X(Ar)}$  values for Mg, Sr, Ba and U. To our knowledge, this study provides the first aragonite  $D_{X(Ar)}$  values determined entirely under cave environmental conditions.

## 2. Cave settings

The data presented here are derived from speleothems from different geographic and environmental settings (Fig. 1): Grotte Prison de Chien and Grotte de Piste (Morocco) (Wassenburg et al., 2012), Mawmluh Cave (Breitenbach et al., 2015) and Krem Umsynrang Cave (NE India), an unnamed cave located 8 km south of Trevélez (S Spain) (Richter et al., 2002), Grotte de Clamouse (S France) (Frisia et al., 2002; McMillan et al., 2005), and Hüttenbläuserschachthöhle (Central Germany) (Jochum et al., 2012; Yang et al., 2015). We emphasize that the settings of these caves cover a wide range of climates varying from summer dry temperate, all year wet temperate, to summer wet temperate conditions (Peel et al., 2007).

For most of the caves, dolostone is a primary host rock component (Table 1). This results in high dripwater Mg/Ca ratios, one of the boundary conditions to precipitate aragonite (Riechelmann et al., 2014). For further details, the reader is referred to Table 1.

### 3. Materials and methods

#### 3.1. Samples

For this study, both lateral and stratigraphic calcite-aragonite (Cc-Ar) transitions from seven speleothems were investigated (Table 1; Fig. 1 and 2). Datasets from Grotte de Clamouse (Frisia et al., 2002; McMillan et al., 2005) as well as Grotte Prison de Chien and Grotte de Piste (Wassenburg et al., 2012) were previously published, and the reader is referred to these publications for a detailed documentation of these samples. In addition, one Cc-Ar transition in each of the stalagmites KRUM11 (Krem Umsynrang Cave), MAW4 (Mawmluh Cave; Breitenbach et al., 2015), and MO (unnamed cave) were analysed. Furthermore, four transitions in stalagmite HBSH1 (Hüttenbläuserschachthöhle; Jochum et al., 2012; Yang et al., 2015) were studied in detail.

Sample KRUM11 is approximately 280 mm long and consists of two parallel stalagmites, which lay on the cave floor when collected. On top of those, a younger, 52 mm long speleothem grew upwards, perpendicularly to the broken precursor sample. The sample exhibits a stratigraphic Cc-Ar transition in the older part of the speleothem and a lateral Cc-Ar transition in the youngest part (Fig. 2). Stalagmite MAW4 is 30 mm long and actively grew at the time of collection in March 2006. MAW4 contains one stratigraphic Cc-Ar transition (Fig. 2). Flowstone MO has a maximum thickness of 74 mm and exhibits multiple stratigraphic and lateral Cc-Ar transitions (Fig. 2). Stalagmite HBSH1 is described in Yang et al. (2015). For all samples, the boundaries between calcite and aragonite mineralogies are macroscopically visible and distinct (Fig. 2).

#### 3.2. Petrography

Aragonite is a polymorph of  $\text{CaCO}_3$  and metastable under Earth surface conditions. Thus, it has a tendency to recrystallize to calcite within months to up to hundred's of thousands of years when exposed to diagenetic fluids (Frisia et al., 2002; Lachniet et al., 2012; Martin-Garcia et al., 2009; Perrin et al., 2014; Zhang et al., 2014). In this study, thin-sections were examined under a polarization microscope in order to assess whether the samples show petrographic evidence for diagenetic alteration. Diagenetic alteration of calcite and aragonite

can be identified by the appearance of dissolution features (Figs. 9c and 10 in Perrin et al., 2014), micritization and aragonite relics (Figs. 3 and 8 in Martin-Garcia et al., 2009) and calcite mosaics (Fig. 14 in Frisia and Borsato, 2010, and Fig. 3 in Scholz et al., 2014). In addition, the mineralogy of the samples was determined by X-ray diffraction at the ETH Zurich, Switzerland, using approximately 30 mg of sample powder, as well as by Raman spectroscopy performed at the University of Mainz, Germany. The Raman spectrometer used was a HR 800 from the company Horiba Jobin Yvon, with an attached Olympus BX41 Microscope equipped with an automatic xyz-stage to undertake the 2-dimensional mappings. A frequency doubled Nd-YAG laser (532.12nm), a grating of 1800 grooves/mm, an entrance slit of 100  $\mu\text{m}$  and a confocal hole of 400  $\mu\text{m}$  were used for the measurements. Every point was measured twice to eliminate spikes; each measurement was performed with an accumulation time of 1 s. To evaluate the calcite content, the intensity of the band at  $282\text{ cm}^{-1}$  was used. For aragonite, the band at ca.  $207\text{ cm}^{-1}$  was used.

### 3.3. Dating

Dating of all samples was performed by the  $^{230}\text{Th}/\text{U}$ -method to assess whether the speleothems grew continuously across the Cc-Ar transitions and to quantify growth rates. Four samples from stalagmite MAW4 were dated at the Minnesota Isotope Laboratory at the University of Minnesota, USA, with a multi-collector inductively coupled plasma mass spectrometer (MC-ICPMS, Thermo Finnigan Neptune-Plus) following the procedures described by Cheng et al. (2000), Cheng et al. (2013), and Edwards et al. (1987). Two samples from stalagmite KRUM11 and four samples from flowstone MO were dated using a Nu Plasma MC-ICPMS at the Max Planck Institute for Chemistry, Mainz, Germany, following the procedures of Obert et al. (2016). The top sample of flowstone MO was dated at the Helmholtz Centre for Ocean Research Kiel (GEOMAR) following the procedure of Fietzke et al. (2005). Eight samples from stalagmite HBSH1 were dated at Bristol University, UK, following the procedures described by Hoffmann et al. (2007). All ages are reported as thousands of years before present (ka BP) with reference to the year 1950 AD.

### 3.4. Trace element analysis

Trace element compositions of sub-samples from speleothems KRUM-11, MAW-4, and MO were analysed at the Max Planck Institute for Chemistry, Mainz, Germany. Mg/Ca, Al/Ca, Si/Ca, P/Ca, Mn/Ca, Sr/Ca, Y/Ca, Ba/Ca, Pb/Ca, Th/Ca, and U/Ca ratios were determined with a Thermo Finnigan Element 2 Inductively Coupled Plasma Mass Spectrometer (ICPMS)



coupled to a New Wave UP213 laser ablation system. The isotopes  $^{25}\text{Mg}$ ,  $^{27}\text{Al}$ ,  $^{29}\text{Si}$ ,  $^{31}\text{P}$ ,  $^{43}\text{Ca}$ ,  $^{55}\text{Mn}$ ,  $^{88}\text{Sr}$ ,  $^{89}\text{Y}$ ,  $^{137}\text{Ba}$ ,  $^{208}\text{Pb}$ ,  $^{232}\text{Th}$ , and  $^{238}\text{U}$  were used. Pre-ablation was performed using an 80  $\mu\text{m}$  spot size at a scan speed of 80  $\mu\text{m/s}$  to clean the sample surface. The line scan technique was employed using a scan speed of 5  $\mu\text{m/s}$  and a 55  $\mu\text{m}$  spot size. Samples were ablated with a pulse rate of 10 Hz and an energy density of 9.5 J/cm<sup>2</sup>. Laser warm-up time (i.e., blank measurement time) was set at 11 s. In order to assess potential sample inhomogeneity, ten individual spot analyses were performed parallel to the line scans at a distance of approximately 100  $\mu\text{m}$  using a 100  $\mu\text{m}$  spot size, an energy density of 10.4 J/cm<sup>2</sup> and a total dwell time of 70 s, including an 11 s blank measurement. Both the line scans and the single spot transects covered the Cc-Ar transitions of interest. Measurements were corrected for background, and  $^{43}\text{Ca}$  was used as an internal standard to convert count rates into trace element/Ca mass ratios, which were then converted into molar ratios in order to calculate distribution coefficients. Relative sensitivity factors were determined using the NIST612 glass and MACS3 CaCO<sub>3</sub> reference materials using the values published in Jochum et al. (2012). In order to avoid matrix effects, Pb was corrected using the relative sensitivity factor derived from MACS3 (Jochum et al., 2012). Three NIST612 and MACS3 analyses, respectively, were performed ca. every hour of sample analysis in order to assess and correct for a potential drift of the mass spectrometer. The line scan data were smoothed with a 5-point-running median. For further information on the methodology and data evaluation, the reader is referred to Jochum et al. (2009; 2012).

The Cc-Ar transitions from stalagmite HBSH1 were analysed at Bristol University, UK. Mg/Ca, P/Ca, Sr/Ca, Y/Ca, Ba/Ca, Pb/Ca, Th/Ca and U/Ca were determined with a NewWave UP193HE Excimer laser coupled to a Thermo Finnigan Element2 ICPMS. The isotopes  $^{26}\text{Mg}$ ,  $^{31}\text{P}$ ,  $^{43}\text{Ca}$ ,  $^{88}\text{Sr}$ ,  $^{89}\text{Y}$ ,  $^{137}\text{Ba}$ ,  $^{208}\text{Pb}$ ,  $^{232}\text{Th}$ , and  $^{238}\text{U}$  were used for analysis. Spots were ablated at 200  $\mu\text{m}$  resolution with a 30  $\mu\text{m}$  spot size. The laser warm-up time was set at 40 s (blank measurement time), followed by 104 s of ablation and 60 s wash-out.  $^{43}\text{Ca}$  was used as an internal standard to convert count rates into concentrations. Samples were ablated with an energy density of 5 J/cm<sup>2</sup> and a pulse rate of 5 Hz. The glass reference materials NIST610 and NIST612 were used for calibration. Data evaluation was performed with the software package “Glitter”.

The uncertainty of the trace element results is represented by the relative standard deviation associated with the mean trace element concentration of the reference materials NIST610 and NIST612 for speleothem HBSH1. For speleothems KRUM11, MAW4 and MO, uncertainties were determined by calculating a mean uncertainty from the individual MACS3 line scans. For speleothem HBSH1, only glass reference materials were measured. Since the

trace element concentrations of these reference materials differ, it is possible to use a different uncertainty for high and low trace element concentrations. This is an advantage considering the difference in trace element concentrations between calcite and aragonite. For an overview, the reader is referred to Table 2. The uncertainties for trace element concentrations in speleothems HK3 and GP2 are based on the MACS1 reference material and were published by Wassenburg et al. (2012).

### 3.5. Derivation of speleothem aragonite distribution coefficients

#### 3.5.1. Approach

Aragonite distribution coefficients were determined using the following procedure: Firstly, we calculated the trace element/Ca ratio of the dripwater feeding the stalagmite using the trace element/Ca ratio of the calcite section of the corresponding Cc-Ar transition and the calcite distribution coefficients (Day and Henderson, 2013). Assuming that the dripwater trace element/Ca ratio did not undergo major changes with time, the speleothem aragonite distribution coefficient can be estimated by combining the trace element/Ca ratio of the aragonite section of the transition and the calculated trace element/Ca ratio of the dripwater.

This approach can be mathematically summarized as follows: The distribution coefficient is a function of the trace element to Ca ratio of the solid divided by the trace element to Ca ratio of the solution (i.e. equation 1). Thus, the calcite distribution coefficient,  $D_{X(Cc)}$ , is given by:

$$D_{X(Cc)} = \frac{X/Ca_{Cc}}{X/Ca_{Solution}} \quad (2)$$

Accordingly, the distribution coefficient for aragonite  $D_{X(Ar)}$  is given by:

$$D_{X(Ar)} = \frac{X/Ca_{Ar}}{X/Ca_{Solution}} \quad (3)$$

$D_{X(Cc)}$  is available from previous studies (Day and Henderson, 2013), and  $X/Ca_{(Cc)}$  and  $X/Ca_{(Ar)}$  are measured values. Using the assumption that the dripwater trace element/Ca ratio was similar for precipitation of calcite and aragonite (see below for a critical discussion),  $X/Ca_{Solution}$  can be calculated from equation (2). Inserting this value in Eq. (3),  $D_{X(Ar)}$  can be calculated. In summary,  $D_{X(Ar)}$  is given by:

$$D_{X(Ar)} = \frac{X/Ca_{Ar}}{X/Ca_{Cc} / D_{X(Cc)}} \quad (4)$$

The calcite distribution coefficients used for the calculations were taken from the cave-analogue precipitation experiments performed by Day and Henderson (2013). These are:  $D_{Mg(Cc)} = 0.01 * e^{0.02 * T}$ ,  $D_{Sr(Cc)} = 0.12$  and  $D_{Ba(Cc)} = 0.11$ . According to the experiments from Day and Henderson (2013), the relation between  $D_{Sr(Cc)}$  and temperature was statistically not significant, for  $D_{Ba(Cc)}$  no relation could be identified either. Day and Henderson (2013) indicate that  $D_{U(Cc)}$  does not show a clear relationship with temperature although the  $D_U$  values for experiments conducted at 7°C and 15°C were slightly different (i.e., 0.11 and 0.12, respectively). Therefore, we estimated cave temperatures during speleothem growth from the literature and cave monitoring data and used the corresponding values for  $D_{U(Cc)}$  and  $D_{Mg(Cc)}$ .

Our approach strongly depends on the validity of the assumption that the trace element/Ca ratio of the dripwater did not undergo a major change during the time covered by the Cc-Ar transition. However, in order to initiate aragonite precipitation, a change in dripwater chemistry is absolutely necessary (Frisia et al., 2002; Riechelmann et al., 2014; Wassenburg et al., 2012). At first glance this seems to be contradictory to our assumption, but if the potential change in dripwater chemistry is accounted for by the uncertainty assigned to the values used for the calculations, the error introduced by our assumption can be propagated to the calculated aragonite distribution coefficients. This is critically discussed in the next section.

### 3.5.2. Error propagation

Because assessing potential past changes in dripwater trace element composition is challenging, speleothem trace element data variability must be considered carefully. In order to solve this, we included the standard deviation of the trace element data in the error propagation of the aragonite distribution coefficients. In addition, the uncertainty of the trace element analysis and the uncertainty related to the published calcite trace element distribution coefficients (Day and Henderson, 2013) are included. The error bars on the calculated aragonite distribution coefficients are, thus, very conservative. We used the following equation to calculate the absolute error of the speleothem aragonite  $D_X$  values:

$$\Delta D_{X(Ar)} = D_{X(Ar)} * \sqrt{\sigma_1^2 + \sigma_2^2 + \sigma_3^2 + \sigma_4^2}, \quad (5)$$

where  $\sigma_1$  is the relative standard deviation determined from the external reference materials (Table 2),  $\sigma_2$  is the relative uncertainty of the calcite distribution coefficient (Day and Henderson, 2013), and  $\sigma_3$  and  $\sigma_4$  are the relative uncertainties of the mean calcite and aragonite trace element to Ca ratios. We note that a potential change in drip water composition during the time that the mineralogy changed from calcite to aragonite remains challenging to assess, therefore we cannot incorporate a fixed uncertainty in the error propagation. However, in the results and interpretation section we discuss the effect of an additional 50% uncertainty of the mean trace element values.

### 3.5.3. Boundary conditions for aragonite precipitation

For precipitation of aragonite in cave environments, specific boundary conditions must be fulfilled. In detail, dripwater pH > 8.2, dripwater Mg/Ca > 0.5, and the calcite saturation index < 0.8 (Riechelmann et al., 2014). However, if dripwater pH < 8.2 or the calcite saturation index > 0.8, calcite will continue to precipitate even though dripwater Mg/Ca > 0.5 (see, for example, drip site BM8 in Bab Maфраque Cave (Riechelmann et al. 2014). Therefore, a change from calcite to aragonite within a speleothem does not always reflect a change in the trace element composition of the dripwater. In addition, calcite and aragonite can co-precipitate from dripwaters with only slightly different chemical composition. This result is corroborated by the existence of lateral Cc-Ar transitions in samples HK1 (Wassenburg et al., 2012), KRUM11 and MO. Therefore, the balance between all three dripwater characteristics (i.e., pH, calcite saturation index, and Mg/Ca) is delicate, and only a small, short-lived (i.e., seasonal - annual) change in one of these parameters can initiate precipitation of aragonite. Furthermore, it is energetically advantageous to continue precipitating the same mineral (termed “syntaxial overgrowth”, Fairchild and Baker, 2012). Thus, the return to the same precipitation conditions does not necessarily initiate calcite precipitation. In short, very minor water chemistry changes could surpass a threshold, triggering a sudden shift from calcite to aragonite. Large shifts in water chemistry are neither required nor necessarily implied.

### 3.6. Sample and trace element data selection

The samples and trace element/Ca ratios selected for the calculations are subject to strict criteria. Post-depositional diagenesis may alter the trace element composition of both aragonite (Lachniet et al., 2012; Ortega et al., 2005) and calcite speleothems (Scholz et al., 2014). Consequently, data derived from diagenetically altered sections were avoided. In addition, only

pure calcite and aragonite phases were used. This is important because even a small amount of co-precipitated calcite (~2%) may have a large effect on the Mg/Ca ratio of aragonite (Wassenburg et al., 2012). Likewise, a small amount of co-precipitated aragonite may have a significant effect on the U/Ca ratio of calcite. Just before and after the change in speleothem mineralogy, co-precipitation of both calcite and aragonite is the rule rather than the exception. Usually, co-precipitation is spatially restricted and causes characteristic spikes in the trace element data. Therefore, the selection of the first datapoint closest to the Cc-Ar transition is based on the absence of spikes in the aragonite Mg/Ca data and the calcite U/Ca data, which are both indicators of co-precipitation. This selection process implies that lateral Cc-Ar transitions are not suitable for determination of distribution coefficients with this strategy because at such sites co-precipitation is very likely to occur. However, due to the slightly higher porosity associated with a larger surface area and higher number of sites for nucleation, it is reasonable to expect that co-precipitation occurs preferentially within aragonite zones. Therefore, the largest offsets are expected for  $D_{Mg(Ar)}$ , whereas the effect should be negligible for  $D_{Sr(Ar)}$ ,  $D_{Ba(Ar)}$  and  $D_{U(Ar)}$  because calcite Sr, Ba and U concentrations are low compared to those in aragonite. Consequently, we use data from two lateral Cc-Ar transitions from stalagmite HK1 (Wassenburg et al., 2012) to verify the values obtained from stratigraphical Cc-Ar transitions in this study. Furthermore, a minimum of several years of trace element data was averaged in order to avoid a bias towards extreme years; at least seven data points are used to calculate the mean X/Ca values for the calcite and aragonite to increase the statistical robustness. This minimum number of points is related to the maximum number of laser spots available for the shortest speleothem section studied (stalagmite HBSH1).

## 4. Results and interpretation

### 4.1. Petrography and degree of preservation

Petrographic studies on the previously published samples indicate that the analysed calcite and aragonite fabrics represent primary mineralogies with only very subtle, if any, diagenetic features (McMillan et al., 2005; Wassenburg et al., 2012). The petrography and degree of preservation of the newly analysed samples is described in the paragraphs below.

#### 4.1.1. Stalagmite MAW4

The calcite portion of stalagmite MAW4 (Fig. 3a-c) shows discontinuous, inclusion-rich layers composed of non-ordered, relatively small (10-100  $\mu\text{m}$  wide) calcite crystals

(Fig. 3b). In between these layers, columnar, radiaxial calcite crystals occur (Neuser and Richter, 2007; Richter et al., 2011) (Fig. 3b). Directly beneath an aragonite interval, calcite fabrics consisting of fan-like structures with a sweeping extinction over several crystals exist (Figs. 3a and 4d).

The aragonite fabrics consist of needle-like crystals, elongated along their c-axis, organized in fans with a sweeping extinction across several crystals (Fig. 3a). This specific type of fabric has been referred to as acicular by Frisia and Borsato (2010). A series of thin brown layers alternating with translucent white layers that are possibly seasonal in origin has been observed, similar to sample MAW-0201 from the same cave (Myers et al., 2015).

The small, non-ordered calcite crystals may represent competitive growth occurring after a growth interruption and are regarded as primary, similar to the columnar, radiaxial calcite. However, the fan-like calcite has a very similar structure as the acicular aragonite. This may represent the product of a fabric-preserving aragonite-to-calcite transformation (Martín-García et al., 2009; Perrin et al., 2014). Therefore, this specific calcite fabric was avoided for the calculations, and only well-preserved columnar calcite fabrics were used. Aragonite fabrics lack signs of micritization, dissolution and aragonite-to-calcite transformation and are thus considered primary.

#### 4.1.2. Stalagmite KRUM11

The calcite fabric of stalagmite KRUM11 appears as mosaic-like in thin sections (Figs. 3d-f) (Frisia and Borsato, 2010), whereas the aragonite directly above the calcite shows an acicular fabric (Frisia and Borsato, 2010) (Fig. 3e). Under plane polarized light, darker, non-translucent zones alternate with translucent crystals within the aragonite (Fig. 3f).

A calcite mosaic fabric is usually interpreted as a result of diagenesis (Frisia and Borsato, 2010; Scholz et al., 2014). However, the calcite did not show any aragonite relicts or dissolution features, and the cross section shown in Figs. 3d-f is not parallel to the c-axis of the crystals, therefore, this calcite was considered to be of primary nature. The aragonite of KRUM11 shows some opaque, non-translucent layers, which appear as micritized aragonite (Fig. 3f). Therefore, this Cc-Ar transition has been excluded for the calculations of the speleothem aragonite distribution coefficients.

#### 4.1.3. Stalagmite HBSH1

The calcite layers within stalagmite HBSH1 are 5-10 mm thick and consist of columnar calcite crystals. The aragonite has an acicular fabric characterised by a sweeping extinction

pattern across several crystals (Fig. 3g). The individual crystals are somewhat longer and wider compared to those from stalagmite MAW4 (Fig. 2), and individual needle-like aragonite crystals and spherulites are distributed between the relatively long and wide aragonite crystals (Fig. 3g). No diagnostic features of diagenesis (e.g., micritization, dissolution or calcite-to-aragonite transformation) are apparent, and the fabrics are therefore considered primary.

#### 4.1.4. Flowstone MO

Flowstone MO consists of an elongated columnar, radiaxial calcite fabric with an undulose extinction (Richter et al., 2011). The aragonite consists of clear, translucent crystals belonging to an acicular fabric (Fig. 3i-j) (Frisia and Borsato, 2010). Both calcite and aragonite do not show any sign of diagenetic alteration, and thus represent primary material.

## 4.2. Conditions of formation

### 4.2.1. Timing of calcite-to-aragonite transitions and determination of speleothem growth rates

Five samples from flowstone MO were dated. Four samples were beyond the dating limit of the  $^{230}\text{Th}/\text{U}$ -method. The top sample was dated at  $106.9 \pm 1.1$  ka (Fig 2; Table 3).

The calcite phase of stalagmite KRUM11 occurred between  $16.89 \pm 0.11$  and  $16.42 \pm 0.12$  ka (Fig. 2; Table 3). The mean growth rate for this section is ca.  $35 \mu\text{m/a}$ .

Sample MAW4 was actively growing at the time of collection (2006 AD). The aragonite samples were dated at  $-0.0476 \pm 0.0018$  and  $-0.0202 \pm 0.0013$  ka (Fig. 2; Table 3), revealing high growth rates with a mean of  $\sim 293 \mu\text{m/a}$ . The two calcite samples were dated at  $0.202 \pm 0.011$  and  $0.395 \pm 0.055$  ka (Fig. 2; Table 3), which corresponds to a much lower mean growth rate of ca.  $24 \mu\text{m/a}$ .

Eight aragonite sub-samples bracketing four Cc-Ar transitions in stalagmite HBSH-1 were dated (Table 3). The corresponding ages are between  $216.6 \pm 2.8$  and  $78.66 \pm 0.81$  ka (Table 3). The corresponding growth rates for the four Cc-Ar transitions are between 1 and  $11 \mu\text{m/a}$ . All growth rates are based on linear interpolation between two subsequent samples.

### 4.2.2. Temperature at time of deposition

Day and Henderson (2013) documented that calcite  $D_{\text{Mg}}$  and  $D_{\text{U}}$  in precipitation experiments depend on temperature. In particular,  $D_{\text{U}(\text{Cc})}$  is 0.11 at  $7^\circ\text{C}$  and 0.12 at  $15^\circ\text{C}$ , whereas  $D_{\text{Mg}(\text{Cc})} = 0.01 * e^{0.02 * T}$ . Although the temperature dependency of  $D_{\text{Mg}(\text{Cc})}$  is relatively

small in comparison to cave site temperature variations, an approximate assessment of cave temperatures is considered important here.

Cave temperature at the time of the Cc-Ar transitions in the investigated samples are estimated using modern cave temperature compiled in the context of cave monitoring programs (Table 1) (Breitenbach et al., 2015; Frisia et al., 2002; Riechelmann et al., 2014; Wassenburg et al., 2013), geographical location of the cave sites (Table 1), and the timing of the growth phases of the Cc-Ar transitions (Table 3). MAW4, KRUM11, HK3, GP2 and CL26 cave air temperatures must have been closer to 15 than to 7°C (Table 4). Thus, we use the higher calcite  $D_U$  of 0.12 (Day and Henderson, 2013). For flowstone MO, the timing of the Cc-Ar transition is unknown, and formation temperature is not quantifiable. However, we use the modern cave air temperature of 13°C for the calculations and, consequently, a  $D_U$  value of 0.12.

Three of the four Cc-Ar transitions from stalagmite HBSH1 grew within the time interval from 131 and 79 ka BP. For each of these transitions, we use a temperature estimate from a pollen and plant macrofossil record from central Germany (Kühl et al. (2007). This record suggests mean January temperatures of -12°C and mean July temperatures of 17.5°C, which corresponds to a mean annual temperature of ~3°C. For the oldest Cc-Ar transition in stalagmite HBSH1, which occurred around 216 ka BP (Marine Isotope Stage 7; Table 3), no temperature estimate can be derived due to a lack of data. Therefore, we assume the same temperature as for the other Cc-Ar transitions from stalagmite HBSH1 (Table 4). Consequently, a  $D_U$  value of 0.11 was used for all four mineralogical transitions found within stalagmite HBSH1.

### 4.3. Distribution coefficients

#### 4.3.1. Trace element data

Trace element data across the Cc-Ar transitions from the different speleothems are presented in Fig. 5. The line scan data reproduce the single spot analyses very well indicating sample homogeneity at the sub-millimeter scale. The Cc-Ar transitions are clearly visible in Mg/Ca, Sr/Ca, Ba/Ca and U/Ca ratios (Fig. 5). As expected, Sr/Ca, Ba/Ca and U/Ca ratios are higher in aragonite, whereas Mg/Ca is higher in calcite. For sample MAW4, a stepwise increase (decrease) in Sr/Ca and U/Ca (Mg/Ca) is apparent starting ca. 3 mm below the Cc-Ar transition and is followed by the actual Cc-Ar transition. A more detailed discussion is required to clarify which data are most useful for the calculations of the aragonite distribution coefficients.



Stalagmite MAW4 shows a fan-like calcite fabric (Fig. 3a-c), which is interpreted as the result of aragonite-to-calcite transformation. It is possible that the intermediate values of Sr/Ca, U/Ca and Mg/Ca are associated with this fabric because it is common that secondary calcite may preserve the trace element signature of the precursor aragonite (Niggemann and Richter, 2006). However, the thin section was taken from another portion of stalagmite MAW4, thus preventing establishing a direct link with the trace element data. Therefore, an area close to the trace element transect was mapped with Raman spectroscopy, which indicated that both phases with the intermediate (Cc1) and high (Cc2) Mg/Ca ratios are indeed calcite with negligible aragonite (Fig. 4). Sr/Ca and U/Ca ratios are higher, and the Mg/Ca ratios are lower in Cc1 than in Cc2, suggesting that aragonite-to-calcite diagenesis may have affected Cc1. Consequently, only the trace element data derived from Cc2 are used to calculate distribution coefficients.

#### 4.3.2. Speleothem aragonite distribution coefficients

The trace element/Ca ratios used to calculate speleothem aragonite  $D_{X(Ar)}$  are shown in Fig. 5 and Table 4. The time represented by each calcite or aragonite trace element value used for the calculation varies from sample to sample, ranging from 2 to 771 years (Table 4). We acknowledge that 771 years seems unreasonably long for the discussion of transitions. However, the corresponding sample (HBSH1-20) has a growth rate of only 1  $\mu\text{m/a}$ , and it is necessary to calculate a mean X/Ca value based on multiple data points to obtain a reliable estimate of both the X/Ca value and its uncertainty for the calculations. For stalagmite MAW4, only the calcite part with the highest Mg/Ca ratios (Cc2) was used in order to prevent a bias due to diagenetically altered calcite (see above).

The calculated aragonite distribution coefficients with associated uncertainties are presented in Table 5 and Fig. 6. The mean aragonite  $D_{Mg(Ar)}$  is  $9.7 \cdot 10^{-5} \pm 9.0 \cdot 10^{-5}$ ,  $D_{Sr(Ar)}$  is  $1.38 \pm 0.53$ ,  $D_{Ba(Ar)}$  is  $0.91 \pm 0.88$ , and  $D_{U(Ar)}$  is  $6.26 \pm 4.53$ .  $D_{X(Ar)}$  values calculated from stalagmite HBSH1 are higher for all elements examined and increase standard deviations significantly (Table 6). This is especially the case for  $D_{Ba(Ar)}$ , which changes from  $0.91 \pm 0.88$  to  $0.46 \pm 0.18$  if the values calculated from stalagmite HBSH1 are excluded (Table 6). Despite the uncertainty, the results demonstrate for the first time that under karst environmental conditions  $D_{Mg(Ar)}$  is considerably smaller than one,  $D_{Sr(Ar)}$  is above one or close to unity, and  $D_{U(Ar)}$  is larger than one. As noted earlier, we used the trace element datasets covering two lateral Cc-Ar transitions from stalagmite HK1 (Wassenburg et al., 2012) to verify the  $D_{Sr(Ar)}$ ,  $D_{Ba(Ar)}$  and  $D_{U(Ar)}$  derived from stratigraphical Cc-Ar transitions. The corresponding  $D_{X(Ar)}$  values are indistinguishable from those derived using stratigraphic Cc-Ar transitions adding

confidence to the validity of our estimates (Fig. 6). The large difference in growth rate between the aragonite (295  $\mu\text{m/a}$ ) and the calcite (24  $\mu\text{m/a}$ ) sections of stalagmite MAW4 does not seem to affect the calculated aragonite  $D_{X(\text{Ar})}$  value because the results are consistent with the other values.

## 5. Discussion

To our knowledge, this is the first attempt to quantify speleothem aragonite  $D_{X(\text{Ar})}$  values (other than the determination of  $D_{\text{U}(\text{Ar})}$  of Jamieson et al. (in revision). Although our approach is relatively simple, the results are consistent for most transitions (in particular for aragonite  $D_{\text{Sr}}$ ) (Fig. 6). This indicates that the incorporation mechanisms are similar for calcite and aragonite, which is a basic requirement for the application of the concept of a distribution coefficient (Fairchild and Treble, 2009). However, the values calculated using stalagmite HBSH1 are higher. Furthermore, the calculated  $D_{\text{Mg}(\text{Ar})}$ ,  $D_{\text{Ba}(\text{Ar})}$  and  $D_{\text{U}(\text{Ar})}$  values show large variability (Fig. 6). Variable environmental conditions and dripwater chemistry characteristics of the different samples may partially explain these differences. Environmental factors, such as temperature, drip rate, precipitation rate, and solution composition, may contribute to the large spread in both calcite and aragonite  $D_X$  values. However, we emphasize that the chemical composition of the dripwaters must have been similar across all transitions because aragonite only tends to precipitate in case of dripwater Mg/Ca ratios  $\geq 0.6$  and dripwater pH  $\geq 8.2$  and a relatively low ( $\leq 0.8$ ) saturation-index with respect to calcite (Riechelmann et al., 2014).

### 5.1. Sensitivity analysis

Although only the best available speleothem samples with calcite-aragonite transitions were used, the calculated aragonite  $D_{X(\text{Ar})}$  values of course depend on the data selected for the calculations. To assess any selection bias, all calculations were repeated with trace element data representing only 2-155 years of stalagmite growth instead of 2-771 years. This transect consisting of 2-155 years of data comprises the part of the original trace element transect of 2-771 years closest to the Cc-Ar transition. This sensitivity analysis was performed on each sample (input parameters used for the corresponding calculations are given in supplemental Table EA1). The median  $D_{X(\text{Ar})}$  values of both datasets are comparable (Table 6), indicating that the calculated  $D_{X(\text{Ar})}$  values do not strongly depend on the selected trace element transect. Nevertheless, the mean X/Ca ratio calculated using the longer dataset should be statistically more robust, and is thus the preferred value.

In addition to varying the number of trace element data points, the results were tested using an aragonite-to-calcite transition from stalagmite HK3 (Wassenburg et al., 2012). We applied the same approach to the data from the Ar-Cc transition to calculate the calcite distribution coefficient by using the aragonite distribution coefficient. Using the same error propagation as for the calculated aragonite distribution coefficients, the calculated calcite distribution coefficients are  $0.019 \pm 0.004$ ,  $0.14 \pm 0.02$ ,  $0.13 \pm 0.02$  and  $0.13 \pm 0.05$  for  $D_{\text{Mg}(\text{Cc})}$ ,  $D_{\text{Sr}(\text{Cc})}$ ,  $D_{\text{Ba}(\text{Cc})}$  and  $D_{\text{U}(\text{Cc})}$ , respectively. Although this transition was interpreted as a hiatus (Wassenburg et al. 2012),  $D_{\text{X}(\text{Cc})}$  values calculated across this transition are, with exception of  $D_{\text{Mg}(\text{Cc})}$ , within error of the  $D_{\text{X}(\text{Cc})}$  values reported by Day and Henderson (2013). We refer to section 5.5 for a detailed discussion of  $D_{\text{Mg}}$ . These cross-validations provide further support that our approach yields reliable results.

## 5.2. Rayleigh distillation effects

Varying amounts of Rayleigh distillation occurring on stalagmite surfaces affect all trace element distribution coefficients in a similar way (Johnson et al., 2006). The amount of Rayleigh distillation controls the apparent  $D_{\text{X}}$  value and depends on (i) drip rate, which controls the mixing between the solution on top of the stalagmite and the impinging drop (Mühlinghaus et al., 2009), and (ii) super-saturation of the dripwater with respect to  $\text{CaCO}_3$ , which controls the precipitation rate. Different drip sites are therefore characterized by varying degrees of Rayleigh distillation and a range of apparent  $D_{\text{X}}$  values. The Rayleigh distillation effect depends on the amount of  $\text{Ca}^{2+}$  that precipitates during a single drip interval, i.e. the excess of Ca. Consequently, drip sites with similar  $\text{CaCO}_3$  deposition rates are characterized by small excess  $\text{Ca}^{2+}$  if (i) drip intervals are short, because there is little time to precipitate  $\text{CaCO}_3$  until replenishment of the water at the top of the stalagmite, (ii) dripwater Ca concentration is high, and (iii) the water film covering the stalagmite surface is thick (because it takes longer for dripwater to reach a higher supersaturation). Here we calculate mean  $\text{CaCO}_3$  deposition rates using the  $^{230}\text{Th}/\text{U}$ -based speleothem growth rates:

$$r = \frac{v \cdot \sigma \cdot 9.48151 \cdot 10^{-4}}{31536000}, \quad (6)$$

where  $r$  is the average  $\text{CaCO}_3$  deposition rate ( $\text{mmol}/\text{cm}^2/\text{s}$ ),  $v$  is the speleothem growth rate ( $\mu\text{m}/\text{year}$ ), and  $\sigma$  is the density of aragonite ( $\text{g}/\text{cm}^3$ ). With assumptions for drip rate, initial

dripwater  $\text{Ca}^{2+}$  concentration and film thickness, the amount of Ca removed from the dripwater per drip can be calculated for every Cc-Ar transition using the equation from Stoll et al. (2012):

$$Ca - excess = \frac{r \cdot \Delta t / \delta}{Ca_i}, \quad (7)$$

where  $\delta$  is the thickness of the water film (cm),  $\Delta t$  is drip interval (s), and  $Ca_i$  is initial Ca concentration ( $\text{mmol/cm}^3$ ). The boundary conditions were chosen relatively conservative, such that the calculated excess  $\text{Ca}^{2+}$  represents an overestimation rather than an underestimation. In particular, we assumed a very long drip-interval of 600 s (10 min), a low initial dripwater Ca concentration of 20 mg/l and a realistic film thickness of 0.01 cm (Baker et al., 2014; Hansen et al., 2013). The estimated amount of excess  $\text{Ca}^{2+}$  precipitation ranges from 0.08 to 3.9% (Table 5), except for stalagmite MAW4 aragonite, for which a value of 19% is estimated. With only 0.08 to 3.9% of excess  $\text{Ca}^{2+}$  precipitation during one drip interval, Rayleigh distillation effects are minimal and within the range of our analytical uncertainties. For MAW4, an influence of Rayleigh distillation on the calculated aragonite  $D_{\text{X(Ar)}}$  values cannot be excluded. However, we emphasize that an initial dripwater Ca concentration of 20 mg/l for the dripwater is very low, and typical values range from 30 to 90 mg/l (Frisia et al., 2002; Karmann et al., 2007; Riechelmann et al., 2011; Tremaine and Froelich, 2013). Drip sites with lower dripwater  $\text{Ca}^{2+}$  concentrations are usually associated with low  $\text{CaCO}_3$  saturation indices and low precipitation rates.

### 5.3. Speleothem aragonite $D_{\text{Sr(Ar)}}$

The aragonite  $D_{\text{Sr(Ar)}}$  values calculated from the different calcite-to-aragonite transitions are in mutual agreement (Fig. 4), with the exceptions of values calculated from HBSH-1 (which are higher than the other values) and stalagmite CL26 (lower than the other values) (Table 4). A comparison with published aragonite  $D_{\text{Sr(Ar)}}$  values shows that the mean value derived from all transitions is in a similar range as the values based on marine analogue laboratory experiments (Table 6).

The calculated aragonite  $D_{\text{Sr(Ar)}}$  values depend on the value used for  $D_{\text{Sr(Cc)}}$  of calcite. Calcite  $D_{\text{Sr(Cc)}}$  is known to be dependent on solution composition (Mucci and Morse, 1983; Pingitore and Eastman, 1986), precipitation rate (Gabitov and Watson, 2006; Treble et al., 2005), and possibly competition effects (Borsato et al., 2007). The latter may be related to the availability of impurities in the crystal lattice, which in turn may be controlled by the

incorporation of Mg. The application of a universal  $D_{Sr(Cc)}$  for all Cc-Ar transitions may therefore not be appropriate.

Precipitation experiments from Mucci and Morse (1983) showed that the incorporation of small sized Mg-ions is accompanied by increasing incorporation of larger Sr-ions. This relationship appeared to be linear and is expressed by  $D_{Sr(Cc)} = 0.146 + 0.01833 * \%MgCO_3$ . Although it is tempting to use this relationship to correct the calcite  $D_{Sr(Cc)}$  values used for the calculations, we do not consider this as a suitable approach since the precipitation experiments from Mucci and Morse (1983) reflect marine conditions. In addition, a calcite  $D_{Sr(Cc)}$  value of 0.146 in absence of Mg seems high in comparison to the values reported from cave precipitation experiments (Tremaine and Froelich, 2013). However, the laboratory precipitation experiments of Day and Henderson (2013) were specifically designed to mimic the solution composition of caves with a limestone host rock, and used dripwater Mg/Ca ratios of 0.047. In our study, the calculated dripwater Mg/Ca ratios of all samples are between 0.6 and 2.8, reflecting the high Mg content of the corresponding host rock (Table 1). Therefore, calcite  $D_{Sr(Cc)}$  may have been generally underestimated resulting in an underestimated value of aragonite  $D_{Sr(Ar)}$ . Since the calcite of HBSH1 is characterized by the lowest Mg/Ca ratios, the aragonite  $D_{Sr(Ar)}$  value calculated from HBSH1 may be least affected by the underestimation of calcite  $D_{Sr(Cc)}$ .

Stalagmite CL26 provided aragonite  $D_{Sr}$  values  $<1$  (0.70; Fig. 6, Table 5). Even considering a calcite  $D_{Sr(Cc)}$  value of 0.15 (McMillan et al., 2005) results in an aragonite  $D_{Sr(Ar)}$  value of 0.87. This value is still lower than the mean value calculated from the four Cc-Ar transitions from stalagmite HBSH1 ( $1.83 \pm 0.46$ ). Considering the relatively similar growth rates of 50  $\mu m/a$  for stalagmite CL26 and 10  $\mu m/a$  for HBSH1, a large growth rate effect on calcite  $D_{Sr(Cc)}$  is unlikely. Furthermore, Pingitore and Eastman (1986) showed that calcite  $D_{Sr(Cc)}$  increases with lower calcite Sr/Ca ratios. However, the calcite Sr/Ca ratios of stalagmite HBSH1 are comparable to those of the other samples (Table 4). Thus, the different values obtained from the different stalagmites may be realistic and explicable by differing factors controlling aragonite  $D_{Sr(Ar)}$ .

Precipitation experiments suggest that aragonite  $D_{Sr(Ar)}$  is higher at lower temperatures, and is defined by  $D_{Sr(Ar)} = 1.27 - 0.005212 * T$  (Dietzel et al., 2004). Stalagmite HBSH1 grew in central Europe during the Last Glacial with an estimated mean annual cave temperature of 3°C. All other samples grew under warmer conditions, i.e., between 12°C and 18°C (Table 4). However, according to the temperature expression from Dietzel et al. (2004), a temperature difference of 10°C would only result in a difference of 0.05 for  $D_{Sr(Ar)}$ , insufficient to explain the observed difference.

Gabitov et al. (2006) reported that Sr incorporation into aragonite shows little dependency on growth rate. However, their experiments were conducted at precipitation rates of 2-117  $\mu\text{m/day}$ , which is not comparable to the slow growth rates of the speleothem samples examined here. Figure 7 suggests a growth rate dependency of aragonite  $D_{\text{Sr}(\text{Ar})}$ , but only for (very) slow growth rates in the range of 1-20  $\mu\text{m/a}$ . For higher growth rates,  $D_{\text{Sr}(\text{Ar})}$  seems to converge to values around 1.01 ( $\pm 0.18$ ), a value that overlaps with the results reported from marine analogue precipitation experiments (Table 6). We emphasize that calcite  $D_{\text{Sr}(\text{Cc})}$  has not been corrected with respect to its Mg/Ca ratio and that the relationship is only based on a small number of data points. In addition, uncertainties in the calculated speleothem growth rate related to dating uncertainties indicate that this suggestion should be considered with caution. Nonetheless, growth rate could be a potential factor, which may be important when interpreting Sr signals of slowly growing aragonite speleothems. Lower growth rates may be associated with higher aragonite  $D_{\text{Sr}(\text{Ar})}$ , contrasting the relationship between growth rate and calcite  $D_{\text{Sr}(\text{Cc})}$ .

#### 5.4. Speleothem aragonite $D_{\text{Ba}(\text{Ar})}$

Both Ba and Sr are characterized by large ionic radii and have similar chemical properties. Therefore, their partitioning into aragonite and calcite is similar. Indeed, precipitation experiments indicate that calcite  $D_{\text{Ba}(\text{Cc})}$  and calcite  $D_{\text{Sr}(\text{Cc})}$  are similar (Day and Henderson, 2013) and increase with increasing growth rates (Tesoriero and Pankow, 1996). Aragonite  $D_{\text{Ba}(\text{Ar})}$  and  $D_{\text{Sr}(\text{Ar})}$  respond in a similar manner to temperature changes, i.e., both Ba and Sr incorporation decrease with increasing temperature (Dietzel et al., 2004; Gaetani and Cohen, 2006). Similarly as for Sr, the relatively large ionic radius of Ba results in preferential incorporation into the aragonite crystal lattice, and aragonite  $D_{\text{Ba}(\text{Ar})}$  is (as  $D_{\text{Sr}(\text{Ar})}$ ) expected to be  $>1$ , at least for temperatures below 40°C (Dietzel et al., 2004; Gaetani and Cohen, 2006) (Table 6). However, only two of our aragonite  $D_{\text{Ba}(\text{Ar})}$  values calculated from Cc-Ar transitions in stalagmite HBSH1 meet this expectation, all other values have a mean of  $0.46 \pm 0.18$  (Table 6; Fig. 6).

Values of aragonite  $D_{\text{Ba}} < 1$  have been reported for temperatures of 40°C and higher (Dietzel et al., 2004; Gaetani and Cohen, 2006). Such temperatures are not expected for cave environments unless they are strongly affected by hydrothermal fluids. Furthermore, aragonite  $D_{\text{Ba}(\text{Ar})}$  seems to be independent of growth rate. As for Sr, solution composition (i.e., high Mg/Ca ratios) and an underestimation of calcite  $D_{\text{Ba}(\text{Cc})}$  may explain this potential underestimation of aragonite  $D_{\text{Ba}(\text{Ar})}$ . The ionic radii of Ca, Sr and Ba in sixfold coordination

are 1.08, 1.21 and 1.44 Å, respectively. Because Ba has the largest ionic radius, increased Mg incorporation may affect calcite  $D_{\text{Ba}(\text{Cc})}$  more strongly than calcite  $D_{\text{Sr}(\text{Cc})}$ , although this idea has not been tested yet. Thus, it remains unclear whether this effect would be sufficient to explain the observed difference with published aragonite  $D_{\text{Ba}(\text{Ar})}$  values derived from precipitation experiments mimicking marine environments. It is possible that in cave environments, Ba incorporation into aragonite is prohibited through competition effects with other large cations. Alternatively, Ba may also be incorporated to a substantial extent through adsorption to colloidal or particulate matter. In summary, our results show that aragonite  $D_{\text{Ba}(\text{Ar})}$  values derived from precipitation experiments reflecting marine environments should be considered with caution when applied to cave environments. Additional work is needed to clarify the incorporation mechanisms in detail.

### 5.5. Speleothem aragonite $D_{\text{Mg}(\text{Ar})}$

Our calculated aragonite  $D_{\text{Mg}(\text{Ar})}$  values agree with the values reported by Gabitov et al. (2008) and Zhong and Mucci (1989) (Table 6), but Gaetani and Cohen (2006) found higher values (Table 6). The discrepancy between Gaetani and Cohen (2006) and other estimates may reflect different experimental setups and analytical techniques (Gabitov et al., 2008). The variability of our calculated speleothem aragonite  $D_{\text{Mg}}$  values is relatively large (Fig. 6), which is most likely related to the incorporation mechanism of Mg into aragonite because its ionic radius in six-fold coordination is only 0.80 Å. Therefore, it is very unlikely to substitute for Ca within the aragonite crystal lattice. Gabitov et al. (2008) found a strong precipitation rate effect and explained it by the growth entrapment model (Watson, 1996, 2004). According to this model, Mg incorporation approaches equilibrium with the solution below a precipitation rate of 0.09  $\mu\text{m}/\text{day}$  (i.e., 33  $\mu\text{m}/\text{a}$ ) (Gabitov et al., 2008), leading to Mg concentrations close to zero ppm. However, the aragonite sections of stalagmite HBSH1 are characterized by growth rates lower than 17  $\mu\text{m}/\text{a}$  and contain 8 ppm Mg. Some studies showed that part of the Mg in aragonite speleothems is associated with Al, Si, and Th, which was interpreted as detrital material (Yang et al., 2015; Wassenburg et al., 2013).

### 5.6. Speleothem aragonite $D_{\text{U}(\text{Ar})}$

Our calculated aragonite  $D_{\text{U}(\text{Ar})}$  values are in a similar range as the relatively high values reported by Meece and Benninger (1993) (Table 6). Furthermore, Jamieson et al. (in revision) also uses speleothem calcite-to-aragonite transitions to calculate  $D_{\text{U}(\text{Ar})}$  and report a value of  $3.74 \pm 1.13$ , confirming our values. In contrast, Gabitov et al. (2008) found significantly lower

aragonite  $D_{U(Ar)}$  values, whereas Kitano and Oomori (1971) reported intermediate values (Table 6). As discussed by Gabitov et al. (2008), U is mostly incorporated into  $CaCO_3$  as  $UO_2(CO_3)_3$  (Reeder et al., 2000), which is most abundant at solution pH-values between 7.5 and 8 (Djogic et al., 1986). For pH-values in this range, high aragonite  $D_{U(Ar)}$  values can thus be expected. However, Meece and Benninger (1993) performed experiments with pH-values between 8 and 8.8, which consequently should result in relatively low  $D_{U(Ar)}$  values. As a consequence, U-incorporation into aragonite must be governed by multiple factors.

The largest speleothem aragonite  $D_{U(Ar)}$  values in our study were derived from stalagmite HBSH1 (Table 6). HBSH1 is the sample with the lowest growth rate, indicating a low supersaturation with respect to  $CaCO_3$  and consequently a low dripwater pH. Compared to the other samples, we thus argue that the pH values of the dripwater associated with stalagmite HBSH1 must have been the lowest, although still high enough to precipitate aragonite (i.e., 8.2, Riechelmann et al., 2014). The relatively high  $D_{U(Ar)}$  values calculated from stalagmite HBSH1 may thus, at least partly, be assigned to the relatively low pH values of the dripwater.

Our calculated speleothem aragonite  $D_{U(Ar)}$  values show a large variability (Fig. 6), which, at least in part, must be assigned to variable calcite  $D_{U(Cc)}$  values used for the calculations. In calcite,  $UO_2$  is likely incorporated in several different configurations and is presumed to have a destabilizing effect (Reeder et al., 2000). Although Kelly et al. (2003) indicated that  $UO_2$  can substitute for Ca within calcite, calcite discriminates more strongly against  $UO_2$ -incorporation compared to aragonite (Reeder et al., 2000). Therefore, we suggest that in calcite speleothems a larger percentage of the bulk U is adsorbed to colloidal phases, of which the incorporation depends on multiple factors (Hartland et al., 2014), which might lead to more variable calcite  $D_{U(Cc)}$  values and thus relatively high variability in speleothem  $D_{U(Ar)}$ .

## 6. Conclusions

Aragonite speleothems may serve as excellent climate archives due to their amenability to  $^{230}Th/U$  dating, provided that potential environmental proxies (i.e., stable isotopes, trace elements) contained within them can be well understood. This study represents a significant improvement towards quantifying and understanding trace element partitioning in speleothem aragonite, which is a prerequisite to assessing the extent to which prior aragonite precipitation (PAP) has affected speleothem aragonite trace element variability. Of special interest is whether  $D_{X(Ar)}$  is above or below one because this determines whether enhanced PAP is associated with lower or higher speleothem trace element concentrations.



We derive mean speleothem aragonite values for  $D_{\text{Mg}(\text{Ar})}$ ,  $D_{\text{Sr}(\text{Ar})}$ ,  $D_{\text{Ba}(\text{Ar})}$ , and  $D_{\text{U}(\text{Ar})}$  of  $9.7 \cdot 10^{-5} \pm 9.01 \cdot 10^{-5}$ ,  $1.38 \pm 0.53$ ,  $0.91 \pm 0.88$ , and  $6.26 \pm 4.54$ , respectively. All estimated values indicate that  $D_{\text{Mg}(\text{Ar})} \ll 1$  and  $D_{\text{U}(\text{Ar})} > 1$  (with the exception of one value), and  $D_{\text{Sr}(\text{Ar})} > 1$  or around unity. For  $D_{\text{Ba}(\text{Ar})}$ , the majority of our samples suggest values  $< 1$ , although a few values are  $> 1$ . Our values show considerable variability, which may be due to variable precipitation rates (particularly important for  $D_{\text{Sr}(\text{Ar})}$  and  $D_{\text{Mg}(\text{Ar})}$ ), pH (important for  $D_{\text{U}(\text{Ar})}$ ), and uncertainties in the calcite  $D_{\text{X}(\text{Cc})}$  used for the calculations. An effect of temperature on  $D_{\text{Sr}(\text{Ar})}$  and  $D_{\text{Ba}(\text{Ar})}$  could not be identified in this study. Furthermore, our data suggest that speleothem aragonite  $D_{\text{Sr}(\text{Ar})}$  may be affected by precipitation rate if the speleothem growth rate is below  $20 \mu\text{m/a}$ . Lower precipitation rates seem associated with higher  $D_{\text{Sr}(\text{Ar})}$ , although this should be confirmed by additional work.

Even though the calculated  $D_{\text{X}(\text{Ar})}$  are associated with considerable uncertainties, this study provides the foundation for interpreting trace element concentrations in speleothem aragonite in terms of climate change. In particular, dry climate conditions may lead to lower karst recharge and enhanced prior aragonite precipitation, which results in lower speleothem U but higher Mg concentrations if prior aragonite precipitation is indeed the dominating process (for example, Jamieson et al., in revision). If  $D_{\text{Sr}(\text{Ar})}$  is above one, then dry climate conditions may also lead to lower speleothem Sr concentrations, although this remains to be confirmed by additional research.

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## Figure captions

Figure 1. Sampling locations of the speleothems used in this study. 1) Grotte Prison de Chien, north-west Middle Atlas, Morocco. 2) Grotte de Piste, north-west Middle Atlas, Morocco. 3) Unnamed cave 8 km south of Treveles, Alpujaras, southern Spain. 4) Grotte de Clamouse, southern France. 5) Hüttenbläuserschachthöhle, central Germany. 6) Krem Mawmluh Cave, Meghalaya plateau, north-east India. 7) Krem Umsynrang Cave, Meghalaya plateau, north-east India.

Figure 2. Slabs showing Cc-Ar transitions with the corresponding trace element transects and the positions of  $^{230}\text{Th}/\text{U}$ -sampling. Blue dashed lines indicate boundaries between calcite and aragonite. Yellow and black arrows indicate speleothem growth direction. a-c) Stalagmite KRUM11. d-e) Stalagmite MAW4. f-g) Flowstone MO. h-i) Stalagmite HBSH1 part 4.

Figure 3. Thin section petrography of calcite and aragonite fabrics. a) Stalagmite MAW4, transition from undulose columnar calcite to calcite fans with sweeping extinction to acicular aragonite. The two calcite fabrics are separated by detrital material (cross-polarised light). b) Stalagmite MAW4, columnar undulose calcite (cross-polarised light). c) Stalagmite MAW4, undulose columnar calcite interbedded by two detrital layers. d) Stalagmite KRUM11, calcite (cross-polarised light). e) Stalagmite KRUM11, Cc-Ar transition with acicular aragonite. (cross-polarised light). f) Same as (e), but with plain polarized light. Arrows indicate primary aragonite (Ar-p) and potentially micritized aragonite (Ar-m). g) Stalagmite HBSH1, part 4, columnar calcite crystals and acicular aragonite (cross-polarised light). h) Same as (g), but with plain polarized light. i) Flowstone MO, undulose columnar calcite crystals and acicular aragonite (cross-polarised light). j) Same as (i), but with plain polarized light.

Figure 4. Results of Raman spectroscopy of stalagmite MAW4. Blue dashed lines indicate the main transition from calcite to aragonite. a) Scan from MAW4 with positions of linescan and spots indicated (red); Cc1 and Cc2 (separated by yellow dashed line) are also indicated. b) 5  $\mu\text{m}$  resolution Raman spectroscopy map covering the aragonite, Cc1 and Cc2. The image is stretched in horizontal direction. c) 2  $\mu\text{m}$  resolution Raman spectroscopy map covering Cc1 with very limited aragonite. Dark red represents aragonite, green represents calcite. d) Thin section of stalagmite MAW4 with Cc-Ar transition (cross-polarised light). e) 2  $\mu\text{m}$  resolution

Raman spectroscopy map covering fan-like calcite and aragonite. Blue represents aragonite, pink represents calcite.

Figure 5. Molar trace element Mg/Ca, U/Ca, Sr/Ca and Ba/Ca ratios across the investigated Cc-Ar transitions. a) Flowstone MO, b) Stalagmite MAW4. c) Stalagmite HBHS1 part 4. Linescan (grey) and single spot (black) analyses, respectively, are indicated. For stalagmite HBHS1, only spot analyses are available. Linescan data are shown as 5-point running medians. Data marked by the red shaded bar represent the data from the calcite section that have been used for the calculations. Data marked by the brown shaded bar represents the data from the aragonite section that have been used for the calculations.

Figure 6. Compilation of the speleothem aragonite distribution coefficients calculated from the Cc-Ar transitions studied. Diamonds (squares) indicate values derived from stratigraphic (lateral) Cc-Ar transitions. Shaded error bars include an additional uncertainty of 50% on the trace element to Ca ratio of the dripwater. Note that the y-axis has a logarithmic scale. For reference, the black horizontal line indicates a distribution coefficient value of 1 for the elements Sr, Ba, and U.

Figure 7. Relation between speleothem aragonite  $D_{Sr}$  and growth rate. Linear regression for the five data points corresponding to growth rates  $< 20 \mu\text{m}/\text{year}$  and associated correlation coefficient and p-value is shown.